

# Non-linear optical spontaneous photoluminescence emission enhancement effect in wide gap gallium nitride thin films

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*With two interfering pulses from the 4<sup>th</sup> harmonic of a Nd-YAG laser we burnt a periodic lattice structure into the surface of GaN thin films. The lattice period of this permanent grating could be controlled between less than one and several tens of microns. Above the decomposition threshold, nitrogen evades from the sample surface, and the residual metallic gallium accumulates in the form of tiny droplets at the surfaces.*

*The patterned structure shows structural similarities with microcavities. The question arises if the residual metallic gallium may act as a partially reflecting mirror.*

*To test this hypothesis, we studied the steady-state and transient photoluminescence through the modulation of light emerging from the ubiquitous broad “yellow” photoluminescence band. The microlattice shows up by energy-equidistant spontaneous emission enhancement peaks in the steady-state photoluminescence spectra. We suggest that the partial reflection due to the residual metallic gallium leads to the observed enhancement effect.*

## Introduction

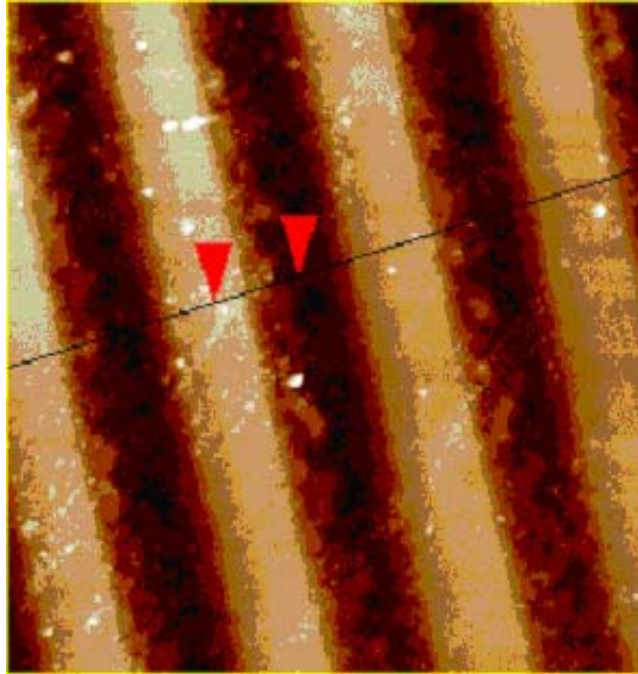
In a pioneering work, Purcell proposed theoretically in 1946 that the spontaneous emission probability is increased and the relaxation lifetime reduced for a system coupled to a resonator [1]. The topic, however, gathered little attention in the posterior decades, as most research was conducted towards induced emission and related laser technology. In 1987, Martini measured lifetime reductions in an optical microcavity under resonant conditions, supporting Purcell's theory with direct experimental evidence [2]. Soon, concepts for the implementation of the enhancement effect in devices were elaborated [3]. The first demonstrated working devices with this new technology were LED's in which the efficiency could be improved significantly through the integration of vertical Bragg reflectors [4]. In gallium nitride and related compounds, vertical microcavities have been employed to study fundamental material properties [5] or the onset of light induced laser emission [6].

Most of the work related to microcavities is based on a *vertical* layered geometry, which takes advantage of the inherent easy control of film thickness in microtechnology. The purpose of this work is to explore an alternative approach, a *horizontal* cavity geometry, which can be introduced by laser interferometric techniques. Laser interferometry can be used to study transient phenomena like free carrier diffusion [7] or to pattern materials [8]. We study lateral burnt-in microcavities in GaN through the modulation of light emerging from the ubiquitous broad “yellow” photoluminescence band.

## Experimental details

Under thermal equilibrium and ambient pressure conditions, solid gallium nitride crystals are decomposed for temperatures above 830 °C into molecular nitrogen gas and liquid gallium. Above this

threshold temperature, the decomposition rate increases exponentially, reaching one monolayer per second at a temperature of 930 °C [8], well below the melting point ( $\approx 2500$  °C). To increase the local temperature above the decomposition threshold we use multiple shots of two crossed focused beams of the 4<sup>th</sup> harmonic (266 nm) of a Nd-YAG laser pulse of duration 5 ns. In accordance with literature [8] we find that the decomposition starts at laser intensities of 220 mJ/cm<sup>2</sup>, and that the single pulse burnt-in depth corresponds approximately to the inverse of the absorption coefficient. The second and subsequent pulses have much lower penetration depths, due to the change of the optical properties with the agglomeration of liquid gallium at the GaN/air interfaces. In our approach, we use multiple shots at a repetition rate of 10 Hz *without* intermediate etching procedures, to allow for thin gallium layers to act as partially reflecting mirrors at the sidewalls of the burnt in trenches. Etching in sulphuric acid was done *after* the PL measurements, and the effect of this procedure on the optical properties was studied.



**Figure 1. Permanent grating surface topography of a  $30 \times 30 \mu\text{m}^2$  area as measured with atomic force microscopy. The height difference between maxima and minima (as indicated by the red arrows) is approximately 240 nm, and the grating period is 8.4  $\mu\text{m}$ .**

The light-induced grating is produced by splitting the excitation pulse of wavelength  $\lambda$  into two parts of equal intensities  $I_0$ , and by focusing both at temporal coincidence onto the sample with a small angle  $\Theta$ . By this way, we generate a grating with fringe spacing  $\Lambda = \lambda / \{2\sin(\Theta/2)\}$ , which is transient for local intensities below, and permanent above the decomposition threshold. For an infinitely sharp decomposition threshold, and in the absence of thermal diffusion effects (effects which of course have to be considered in general), one expects for a two dimensional (with a length coordinate  $x$  and a depth coordinate  $z$ ) sinusoidal intensity grating  $I(x,z) = I_0 (1-R)\{1+\cos(\pi x / \Lambda)\}$  a *rectangular* permanent grating. Besides the main period  $\Lambda$ , we have secondary length scales defined

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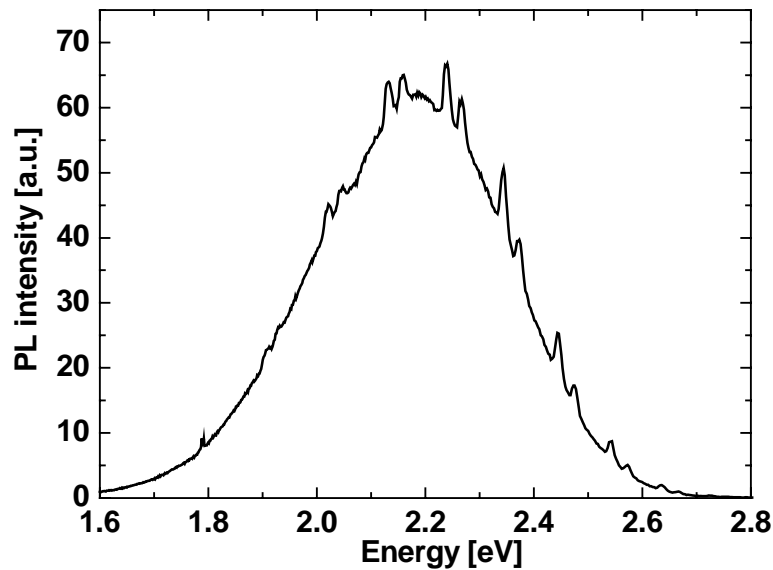
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by the ratio of the maximum laser intensity to the material-dependent decomposition threshold intensity.

The resulting surface morphology was studied with a commercial atomic force microscope (AFM). Photoluminescence (PL) measurements were carried out with a 325 nm cw He-Cd laser and the excitation power density was typically less than  $0.6 \text{ Wcm}^{-2}$ . We restricted ourselves to room temperature measurements. A 325 nm band pass filter was used to attenuate lines other than the 325 nm laser line. The luminescence was dispersed by a Spex 1704 monochromator (1m, 1200/mm) and detected by a Hamamatsu R928 photomultiplier.

## Results

In figure 1 we show the AFM surface topography of a  $30 \times 30 \text{ }\mu\text{m}^2$  area on the top of a permanent grating which was burnt-in with the multi-pulse technique described above. The height difference between maxima and minima (as indicated by the arrows) is approximately 240 nm, and the grating period is  $8.4 \text{ }\mu\text{m}$ . Prior to the AFM measurement shown in figure 1 the liquid gallium was removed from the sample surface in a chemical wet etching procedure. Otherwise, due to strong height differences caused by gallium droplets, the measurement could not be done reliably. Most top and bottom regions show some kind of flat mesa structures. However, the dominating topography is better described by a sinusoidal with a sharp sidewall steepness. This is in accordance with literature where a sinusoidal surface morphology after multipulse etching was reported [8]. The trenches are deeper as expected from a single pulse ( $1/\alpha \approx 100 \text{ nm}$ ), but clearly do not scale with the number of shots. It seems that a UV absorbing liquid metallic gallium layer protects the GaN layer from further decomposition.



**Figure 2.** Room temperature PL measurement of the yellow luminescence band excited on the top of the permanent grating structure. A periodic modulation structure of narrow double peaks is seen, which can be attributed to multiple reflections inside the Fabry-Perot microcavity.

In figure 2 we show a room temperature PL measurement of the yellow luminescence excited on the top of the permanent grating structure before etching. A periodic modulation structure of narrow double peaks appears on the top of the well-known yellow luminescence band centred at approximately 2.2 eV. The energy spacing of adjacent doublets is  $\Delta E = 105 \pm 1 \text{ meV}$ , the separation of the two doublet peaks is 30 meV. Individual peaks are symmetric, with a Lorentzian line shape, with nearly energy independent full width of half maximum (FWHM) of 15 meV. This value, well below the limit of thermally limited line broadening (which at ambient temperatures should be about  $1.8 \cdot kT \approx 47 \text{ meV}$ ), is a hint for the interferometric nature of the peaks.

The yellow band is asymmetric, and its properties can be understood in terms of two independent transitions (sometimes referred to as yellow and green luminescence), each of which is contributing a Gaussian to the total spectral PL [9]. The best fit in the frame of this model results in a yellow component with mean at  $E_{p1} = 2.1 \text{ eV}$  and  $\text{FWHM}_{p1} = 0.35 \text{ eV}$ , and a green component at  $E_{p2} = 2.25 \text{ eV}$  and  $\text{FWHM}_{p2} = 0.3 \text{ eV}$ . These fits are good up to an electron energy of about 2.7 eV, where the blue luminescence band starts.

In order to determine the experimental spectral spontaneous emission enhancement (SEE), we first subtract the baseline by subtracting the double Gaussian band from the experimental data, and then renormalize it by division through the sum of the two Gaussians, which describes the yellow band. This is justified by the fact that the maxima of the enhancement peaks should be proportional to the YL band intensity. Finally, the values have to be added to unity. As a result we show the experimentally determined values for the spontaneous emission enhancement in figure 3.

## Discussion

An important figure-of-merit for the discussion of Fabry-Perot microcavities is the finesse  $F$ . For a low loss one-dimensional optical cavity consisting of two coplanar reflectors with reflectivities  $R_1$  and  $R_2$ , the finesse  $F$  is defined in equation 1 :

$$F = \pi \frac{\sqrt{R_1 \cdot R_2}}{1 - R_1 \cdot R_2} = \frac{\Delta E}{\delta E} \quad (\text{Equation 1})$$

The first term relates the finesse  $F$  to the microcavities inherent properties; the second one connects it to the measured spectra through the mode separation  $\Delta E$  and the single mode linewidth  $\delta E$ . Equation 1 can be used to find the finesse  $F$  from the experimental linewidth of the peaks respective doublet separation. The measured peak heights are apparent values and cannot be used in this procedure. From the values measured in figure 5 we calculate a finesse  $F \approx 24$  and a round trip reflectivity  $R_1 \cdot R_2 = 0.88$ . Taking into account the simple experimental arrangement, these values are surprisingly high.

The spontaneous emission (SE) probability under resonant conditions in a low loss microcavity is enhanced to its maximum by a factor given by the finesse  $F$ . The same parameter broadens the peak linewidth in the Airy function, which is most adequate to describe the SE spectral dependence:

$$SE(E) \propto \frac{1}{1 + F \cdot \sin^2(\pi E / \Delta E)} \quad (\text{Equation 2})$$

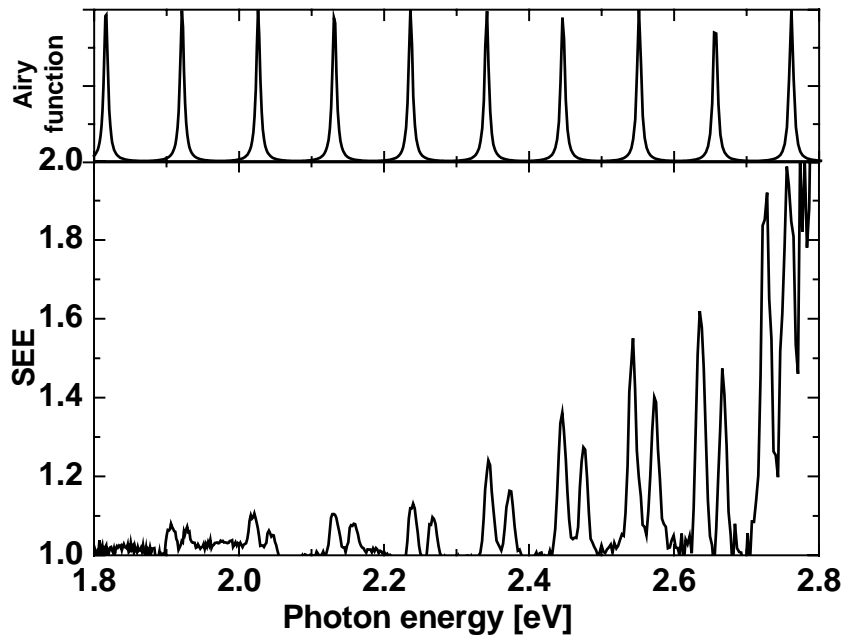
A plot of equation 2 is given in the upper part of figure 3.

The following equation correlates the peak separation  $\Delta E$  to the burnt in grating period  $\Lambda$

$$\Delta E = \frac{1.24}{2n\Lambda} \quad (\text{Equation 3})$$

Here,  $\Delta E$  has to be used in eV and  $\Lambda$  in microns. Assuming a constant refractive index of  $n = 2.4$ , one calculates for the experimental value  $\Delta E = 105 \text{ meV}$  a grating period of  $\Lambda = 2.7 \text{ }\mu\text{m}$ , well below the nominal resonator thickness  $\Lambda/2 = 8.4/2 \text{ }\mu\text{m}$ , as measured with AFM. The difference can be explained taking into account the thickness of the metallic gallium mirrors at the sidewalls of the burnt-in trenches, and should therefore be considered an effective optical resonator thickness.

Regarding the spectral dependence of the apparent spontaneous emission enhancement (SEE) factor as shown in fig. 3. it is obvious that the enhancement is far from the value of the finesse  $F = 24$ . However, we measure a superlinear increase of SE for increasing photon energy, with values near to 2 at the reliable upper energy limit of about 2.7 eV.



**Figure 3. Apparent experimental spontaneous emission enhancement (bottom) and calculated Airy function (top)**

Two comments are in order. First, the strong reduction of the resonant SEE values in fig. 3 compared to  $F = 24$  is most likely due to low optical outcoupling efficiencies. And, secondly, the strong spectral dependence of the resonant SEE values is correlated to scatter effects.

The doublet structure, in our interpretation, arises from additional reflections inside the microcavity. As mentioned before, considering a sharp decomposition threshold, we expect a nested structure inside the main lattice period  $\Lambda$ , which can give rise to additional sidewalls and reflections. This sub-cavity would introduce an apparent phase shift into the PL spectra, what is in fact observed. The separation of the doublet peaks should therefore be correlated with the surface topography from figure 1. This is not the case, which we attribute to the fact that the AFM graph shows only a small region of the excited PL area. Phonon replica with a typical zero centre LO phonon energy of 92 meV are incompatible as the source of the observed YL modulation.

From an experimental point of view we want to point out that the etching step and the resulting structure of the liquid gallium inside the trenches seem to be the key for successful measurements. Presently, few information is available concerning the microscopic structure of the metallic gallium after the evaporation of molecular nitrogen, as most work is concerned with clean GaN layers. The exact light induced etching procedure is critical. It is curious that the enhancement effect disappears after a chemical wet etching step and gallium removal.

## Conclusions

We have observed a periodic modulation of the yellow luminescence in GaN on the top of a permanent holographic grating that was burnt into the GaN film by thermal decomposition through two interfering laser beams. We interpreted the modulation as the resonance modes in a lateral Fabry Perot microcavity. We deduced a finesse value of  $F = 24$  and discussed the apparent increase of the resonant spontaneous emission as a geometric effect.

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